Solubility and Diffusivity Data for the Absorption of COS, CO2, and N2O in Amine Solutions

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Published in:
Journal of Chemical & Engineering Data

DOI:
10.1021/je00005a017

Publication date:
1992

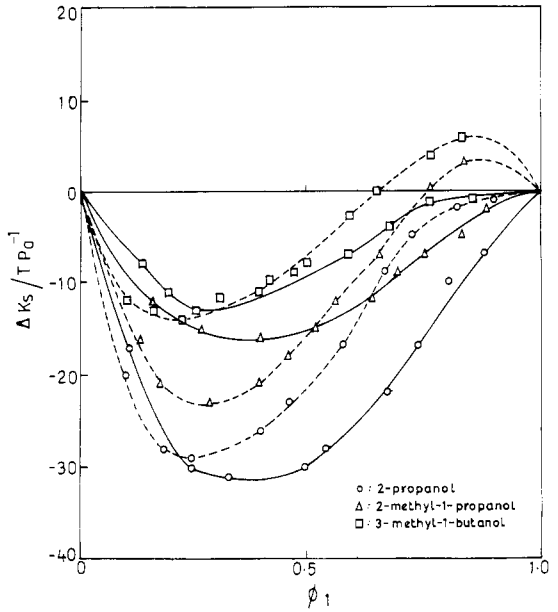

Figure 2. Δk_s plotted against volume fraction (ϕ_1) of *p*-chlorotoluene at 303.15 K (—) for *p*-chlorotoluene (1) + (O) 2-propanol (2), (Δ) 2-methyl-1-propanol (2), and (□) 3-methyl-1-butanol (2) and (- -) for *p*-chlorotoluene (1) + (O) 1-propanol (2), (Δ) 1-butanol (2), and (□) 1-pentanol (2).

k_s, $k_{s,1}$, and $k_{s,2}$ are the isentropic compressibilities of a mixture and the pure components 1 and 2, respectively. ϕ_1 and ϕ_2 are the volume fractions of the components. The values of k_s and Δk_s are also given in Table IV. The results are shown in Figure 2 along with those for mixtures of *p*-chlorotoluene with 1-propanol, 1-butanol, and 1-pentanol.

The isothermal compressibility results also have been fitted into an empirical equation of the form

$$\Delta k_s = \phi_1\phi_2[b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \quad (6)$$

The values of the constants b_0, b_1, and b_2 are included in Table V, along with the standard deviations $\sigma(\Delta k_s)$.

Excess volume data included in Table II show that the excess function exhibits a sign inversion for the three mixtures. However, positive values of V^E dominate over a large range of concentration of *p*-chlorotoluene. Figure 1 indicates that the replacement of 1-alcohols by isoalcohols leads to an increase in algebraic value of V^E.

Results included in the Table IV indicate that Δk_s is negative over the whole range of composition. Figure 2 shows that the replacement of 1-alcohols by isoalcohols does not lead to a significant change in this property.

Registry No. *p*-Chlorotoluene, 106-43-4; 2-propanol, 67-63-0; 2-methyl-1-propanol, 78-83-1; 3-methyl-1-butanol, 123-51-3.

Literature Cited

(1) Sivakumar, K.; Naidu, P. R. *J. Chem. Eng. Data*, submitted for publication.
(2) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788-90.
(3) Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
(4) Vogel, A. *A Textbook of Practical Organic Chemistry*; Longman English Language Book Society: Birmingham, AL, 1978; p 698.
(5) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: New York, 1950.
(6) *Kirk-Othmers' Encyclopedia of Chemical Technology*; 3rd ed.; Wiley-Interscience: New York, 1979; p 820.

Received for review March 13, 1991. Accepted September 27, 1991.

Solubility and Diffusivity Data for the Absorption of COS, CO_2, and N_2O in Amine Solutions

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Absorption data for COS and N_2O in aqueous solutions of *N*-methyldiethanolamine (MDEA), ethylene glycol, and sulfolane (tetrahydrothiophene 1,1-dioxide) at 298 K and solubility data for COS in water at temperatures ranging from 298 to 338 K are presented. Also density, viscosity, N_2O solubility, and N_2O diffusivity data are reported for a wide range of aqueous alkanolamine solutions, aqueous mixtures of alkanolamines, and solutions of MDEA in water/ethanol. It is shown that an analogy between COS and N_2O with respect to gas solubility in aqueous solutions of ethylene glycol and sulfolane holds up to about 25 mass %. This seems to justify, for engineering purposes, the application of this analogy for the estimation of COS solubilities in diluted aqueous amine solutions. Direct verification of a COS-N_2O analogy was provided by absorption of N_2O and COS into aqueous MDEA solutions in a laminar film reactor.

1. Introduction

Alkanolamine processes are one of the most frequently applied processes for the removal of acid components like H_2S, COS, and CO_2 from industrial and natural gases. Diethanolamine (DEA), diisopropanolamine (DIPA), and *N*-methyldiethanolamine (MDEA) are industrially well-known alkanolamines for gas-treating purposes (*1*). Apart from mass-transfer and kinetic data, physical data like gas diffusivity and solubility are also required for an adequate design of gas-treating plants. These data are also necessary in the deduction of chemical reaction kinetics from absorption experiments. However, due to chemical reactions, these physical constants can usually not be measured in a direct way.

For CO_2 the analogy with N_2O is widely applied to estimate the solubility and diffusivity in aqueous alkanolamine solutions. N_2O is similar to CO_2 with regard to configuration, molecular volume, and electronic structure but does not react with alkanolamines. The CO_2-N_2O analogy states that the ratio of the solubilities of CO_2 and N_2O in water is the same as the ratio of the solubilities of both gases in the alkanolamine solution:

$$(m_{CO_2}/m_{N_2O})_{am.\ soln} = (m_{CO_2}/m_{N_2O})_{H_2O} \quad (1)$$

Laddha et al. (*2*) showed that the CO_2-N_2O analogy holds for various aqueous solutions of alcohols. Haimour and Sandall (*3*) studied the absorption of CO_2 and N_2O into aqueous MDEA solutions at various temperatures in a laminar liquid jet. Due

0021-9568/92/1737-0049$03.00/0

to the very short contact times in this type of reactor, the absorption of CO_2 could be considered as physical absorption without any enhancement as a result of the chemical reaction between CO_2 and MDEA. Therefore they were able to verify the CO_2–N_2O analogy for both solubility and diffusivity (combined in the parameter $mD^{1/2}$) for aqueous MDEA solutions up to MDEA concentrations of 1710 mol/m^3.

Al-Ghawas et al. (*4*) suggested a similar analogy between COS and N_2O, although COS and N_2O are less similar than CO_2 and N_2O. They reported $mD^{1/2}$ values for COS and N_2O in water, 15.5 mass % ethylene glycol, and 2570 mol/m^3 MDEA. For all three systems the ratio between the $mD^{1/2}$ values of COS and N_2O was constant within the experimental accuracy.

In the present work this COS–N_2O analogy is investigated more extensively. Absorption data for COS and N_2O in aqueous solutions of MDEA, ethylene glycol, and sulfolane (tetrahydrothiophene 1,1-dioxide) at 298 K and solubility data for COS in water at temperatures ranging from 298 to 338 K are presented. Also density, viscosity, N_2O solubility, and N_2O diffusivity data are reported for various aqueous alkanolamine solutions, aqueous mixtures of alkanolamines, and solutions of MDEA in water/ethanol.

2. Experimental Section

Density measurements were carried out either with calibrated 10-mL pycnometers submerged in a thermostated water bath or with a PAAR DMA58 densitymeter. The viscosities of the various solutions were measured by means of calibrated Ubbelohde viscosimeters which were submerged in a thermostated water bath. The experimental errors in density and viscosity measurements were estimated to be equal to ±0.05 kg·m^{-3} and ±10^{-6} Pa·s, respectively.

For solubility measurements two types of thermostated stirred vessels were applied. All COS solubility experiments were carried out in a vessel with a high-intensity gas stirrer which allowed the contents to reach vapor–liquid equilibrium within about 30 s. In this way any influence of the COS hydrolysis reaction with water was avoided, as can be concluded from the COS hydrolysis rates published by Philipp and Dautzenberg (*5*). Most of the N_2O solubilities were measured in stirred cell reactors identical to those applied in reaction kinetics experiments (*6*–*8*). Both types of stirred vessels had a total volume of about 1250 mL. Detailed information concerning the experimental procedure can be found elsewhere (*6*, *9*). The reproducibility of the solubility measurements was better than 4%.

The diffusivity experiments were carried out in a laminar film reactor. Experimental setup and procedure was essentially identical to those described by Nijsing et al. (*10*). For the absorption of COS into aqueous MDEA solutions, condition 2 should be fulfilled in order to avoid the absorption flux being affected by the reaction between COS and MDEA.

$$Ha = \frac{(k_{app}D_{COS})^{1/2}}{k_L} < 0.2 \qquad (2)$$

COS reacts extremely slowly with MDEA in aqueous solutions; for the highest amine concentration applied in the present diffusion experiments, the K_{app} can be estimated from the work of Littel et al. (*11*) to be lower than 0.1 s^{-1}. Since short contact times, resulting in high k_L values (about 10^{-4} m·s^{-1}), can be achieved in a laminar film reactor, condition 2 could be satisfied for all diffusivity experiments. The experimental accuracy of the diffusivity measurements was estimated to be about 10%. For all diffusivity experiments, highly pure MDEA was used in order to avoid any influence of rapidly reacting contaminants (i.e. primary and secondary amines) on the absorption flux.

In the present work all amines used were at least 99% pure and obtained from Janssen Chimica (MEA, DEA, MMEA, AMP, morpholine, TEA, MDEA, DMMEA), Merck (DEMEA), Texaco Chemical (DGA), and Riedel-de Haën (DIPA). Commercial grade sulfolane was provided by Shell.

The water content in the ethylene glycol/water, sulfolane/water, and MDEA/ethanol/water mixtures was determined by means of a Carl-Fisher titration. Amine concentrations in aqueous solutions of a single amine were analyzed with a standard acid–base titration. Secondary and tertiary amine concentrations in aqueous blends of amines were determined by means of the titration method described by Siggia et al. (*12*).

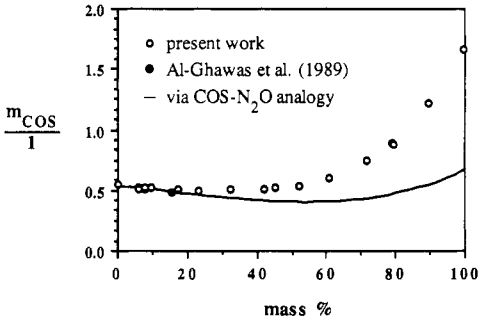

Figure 1. COS solubilities as a function of ethylene glycol concentration at 298 K.

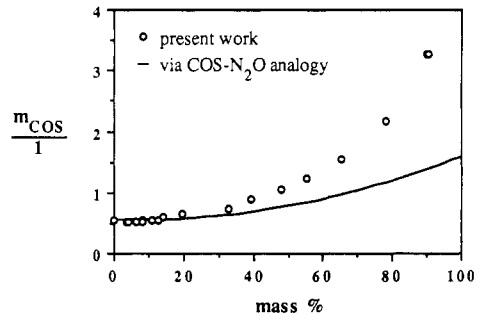

Figure 2. COS solubilities as a function of sulfolane concentration at 298 K.

3. Results

3.1. COS–N_2O Analogy. COS and N_2O solubilities in aqueous solutions of ethylene glycol and sulfolane have been determined at 298 K in order to investigate the validity of a COS–N_2O analogy. The experimental data are presented in Tables I and II. The present N_2O solubilities in aqueous ethylene glycol solutions are in good agreement with the data published by Oyevaar et al. (*13*). In order to validate an analogy between COS and N_2O, the present N_2O solubility data were used to estimate COS solubilities

$$(m_{COS})_{sol.} = (m_{N_2O})_{sol.}(m_{COS}/m_{N_2O})_{H_2O} \qquad (3)$$

with the solubility m defined as the ratio of liquid-phase and gas-phase concentrations of the solute gas at equilibrium conditions:

$$m_{COS} = ((C_{COS})_{liq}/(C_{COS})_{gas})_{equil} \qquad (4)$$

In Figures 1 and 2, experimentally determined COS solubilities are presented together with COS solubilities calculated according to relation 3. From these figures it can be concluded that calculation of COS solubilities from N_2O solubility data via a COS–N_2O analogy is valid up to concentrations of about 25 mass % ethylene glycol and sulfolane. This seems to validate satisfactorily the assumption of such an analogy for COS solubilities in diluted aqueous solutions of alkanolamines.

A direct check of the validity of the COS–N_2O analogy for the combined parameter $mD^{1/2}$ is provided by absorption of COS and N_2O into an aqueous solution of a slowly reacting amine carried out in an absorption apparatus with a high specific mass-transfer rate. In Table III, $mD^{1/2}$ values at 298 K for

Table I. Solubility Data for COS and N_2O in Ethylene Glycol (ETG)/Water Mixtures at 298 K

ETG/(mass %)	m_{COS}	m_{N_2O}	ref
5.8	0.521		present work
5.9	0.511		present work
7.6	0.515		present work
7.8	0.518		present work
9.5	0.517	0.568	present work
9.5		0.571	13
15.5	0.488	0.571	4
17.4	0.506	0.555	present work
17.4		0.541	13
23.1	0.491		present work
23.3	0.500		present work
32.4	0.516	0.497	present work
32.4		0.477	13
41.9	0.509		present work
42.0	0.513		present work
45.1	0.518	0.480	present work
45.1		0.451	13
51.9	0.539		present work
60.6	0.595	0.479	present work
60.6		0.454	13
71.7	0.745	0.492	present work
71.7		0.482	13
79.1	0.889		present work
79.3	0.880		present work
89.6	1.210		present work
99.7	1.658	0.746	present work
99.7		0.735	13

Table II. Solubility Data for COS in Sulfolane/Water Mixtures at 298 K

sulfolane/ (mass %)	ρ/ (kg·m^{-3})	η/ (10^{-3} Pa·s)	m_{COS}	m_{N_2O}
3.6			0.513	
4.1			0.517	
6.2			0.527	
8.1			0.537	
8.2			0.534	
8.9				0.598
11.1			0.546	
11.8				0.610
12.8	1023.5	1.00	0.552	
14.1			0.602	
16.6				0.630
19.5	1041.3	1.11	0.663	
22.2				0.637
30.4				0.686
32.7	1071.6	1.32	0.738	
39.4	1094.1	1.51	0.898	
45.4				0.792
47.9	1116.7	1.74	1.048	
55.1			1.220	
60.9				0.966
65.4	1163.2	2.52	1.549	
76.1				1.257
78.2			2.162	
89.8	1228.0	5.19	3.275	
90.3			3.256	

Table III. $mD^{1/2}$ for COS in Aqueous MDEA Solutions at 298 K

MDEA/ (mol·m^{-3})	gas	$mD^{1/2}$/ (10^{-5}m·s$^{-0.5}$)	ref
0	COS	2.28	14
0	COS	2.20	4
0	COS	2.05	present result
190	COS	1.93	present result
470	COS	1.69	present result
708	COS	1.69	present result
922	COS	1.79	present result
2570	COS	1.50	4

COS in water and various aqueous MDEA solutions, measured in a laminar film reactor, are presented together with previously reported values (*4*, *14*). In Figure 3, experimentally determined

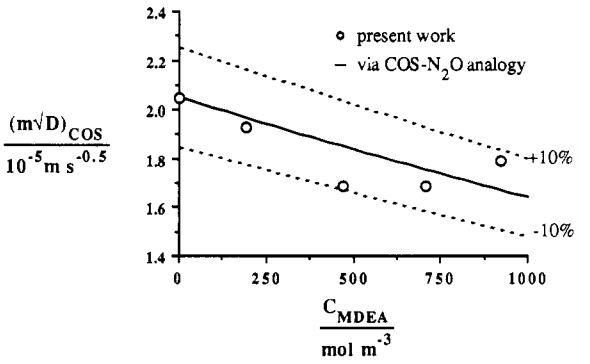

Figure 3. $mD^{1/2}$ values for COS in aqueous MDEA solutions at 298 K.

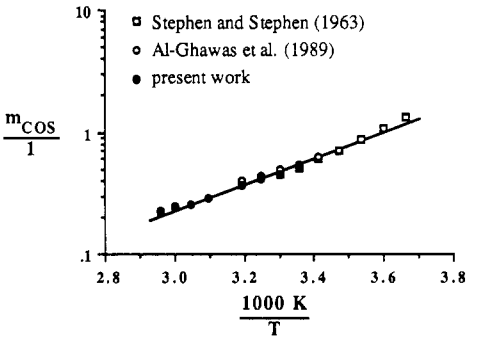

Figure 4. COS solubilities in water.

Table IV. Solubility of COS in Water at Various Temperatures

T/K	m_{COS}	ref	T/K	m_{COS}	ref
273	1.333	15	303	0.457	present study
278	1.075	15	308	0.440	4
283	0.867	15	308	0.412	present study
288	0.714	15	313	0.395	4
288	0.714	4	313	0.362	present study
293	0.602	15	313	0.369	present study
293	0.621	4	323	0.284	present study
298	0.511	15	323	0.287	present study
298	0.539	4	328	0.255	present study
298	0.544	present study	333	0.245	present study
298	0.547	present study	333	0.242	present study
303	0.447	15	338	0.227	present study
303	0.498	4	338	0.221	present study
303	0.456	present study			

$(mD^{1/2})_{COS}$ values and $(mD^{1/2})_{COS}$ values calculated from $(mD^{1/2})_{N_2O}$ values (*9*) via the COS–N_2O analogy are presented. From this figure it can be concluded that fair agreement exists between calculated and estimated $mD^{1/2}$ values, especially if a reproducibility of about 10% inherent to the experimental method is taken into account. The $mD^{1/2}$ values reported by Al-Ghawas et al. (*4*) for water and 2570 mol/m^3 MDEA are both somewhat higher than the present results. Moreover, it should be noted that the $mD^{1/2}$ data published by Al-Ghawas et al. (*4*) show at higher temperature significant discrepancy with the data reported by Haimour and Sandall (*3*) and Versteeg and Van Swaaij (*9*), whereas at 298 K satisfactory agreement exists.

In Table IV and Figure 4, solubility data for COS in water at various temperatures are presented. From these data it is clear that good agreement exists between the present data and the data reported by Stephen and Stephen (*15*) and Al-Ghawas et al. (*4*). The temperature dependence of the COS solubility in water can be described by an Arrhenius relationship:

$$m_{COS} = 2.33 \times 10^{-4} \exp(2308/T) \quad (5)$$

Relation 5, together with N_2O solubilities in water and aqueous amine solutions, offers the possibility of estimating ac-

Table V. Polynomial Coefficients for the Calculation of the Density ρ of Aqueous Alkanolamine Solutions of Concentration C at Various Temperatures [$\rho/(\text{kg}\cdot\text{m}^{-3}) = a_0 + a_1(C/(\text{mol}\cdot\text{m}^{-3})) + a_2(C^2/(\text{mol}^2\cdot\text{m}^{-6})) + a_3(C^3/(\text{mol}^3\cdot\text{m}^{-9}))$]

amine	T/K	C_{max}/(mol·m^{-3})	a_0	10^3a_1	10^6a_2	10^9a_3
MEA	303	4943	995.7	1.944	0.139	
MEA	318	4906	990.3	1.701	0.087	
MEA	333	4864	983.2	1.456	0.078	
MEA	348	4782	975.0	1.484	0.027	
DGA	298	6140	998.6	9.868		
DGA	303	4084	995.5	9.626		
DGA	318	4758	990.2	8.673		
DGA	333	4709	983.2	8.015		
DEA	303	4828	995.6	11.92		
DEA	318	4791	990.2	11.47		
DEA	333	3224	983.2	8.151	1.295	
MMEA	293	4789	998.2	−1.386	0.757	−0.072
MMEA	303	4762	995.7	−1.564	0.602	−0.061
MMEA	318	4718	990.3	−1.702	0.378	−0.043
MMEA	333	3288	983.4	−1.733	0.111	
AMP	303	5009	995.7	−2.342	1.130	−0.176
MOR	303	3897	995.5	5.998		
TEA	293	2408	998.0	23.04		
TEA	303	2398	995.1	22.41		
TEA	318	2382	990.1	21.64		
TEA	333	2363	983.8	21.19		
DMMEA	303	2387	995.2	−3.113		
DMMEA	318	2368	989.6	−4.120		
DMMEA	333	2346	983.5	−5.144		
DEMEA	293	2369	997.9	−2.814		
DEMEA	303	2354	995.4	−4.466		
DEMEA	318	2332	990.3	−6.318		
DEMEA	333	2305	984.4	−8.453		

Table VI. Polynomial Coefficients for the Calculation of the Viscosity of Aqueous Alkanolamine Solutions at Various Temperatures [$\eta/(10^{-3}\ \text{Pa}\cdot\text{s}) = b_0 + b_1(C/(\text{mol}\cdot\text{m}^{-3})) + b_2(C^2/(\text{mol}^2\cdot\text{m}^{-6})) + b_3(C^3/(\text{mol}^3\cdot\text{m}^{-9}))$]

amine	T/K	C_{max}/(mol·m^{-3})	b_0	10^3b_1	10^6b_2	10^9b_3
MEA	303	4943	0.797	0.097	0.030	
MEA	318	4906	0.598	0.073	0.017	
MEA	333	4864	0.467	0.051	0.010	
MEA	348	4782	0.378	0.035	0.007	
DGA	298	6140	0.857	0.478	−0.097	0.044
DGA	303	4084	0.810	0.096	0.132	
DGA	318	4758	0.595	0.204	−0.009	0.013
DGA	333	4709	0.467	0.124	0.005	0.006
DEA	303	4828	0.793	0.350	−0.050	0.045
DEA	318	4791	0.594	0.228	−0.022	0.023
DEA	333	3223	0.473	0.080	0.055	
MMEA	293	2400	1.000	0.409	−0.088	0.053
MMEA	303	4762	0.798	0.208	0.024	0.010
MMEA	318	4718	0.596	0.152	0.004	0.007
MMEA	333	3288	0.468	0.079	0.023	
AMP	303	3979	0.800	0.322	0.0235	0.027
MOR	303	3897	0.798	0.197	0.027	0.008
TEA	293	2408	1.043	0.191	0.373	
TEA	303	2398	0.831	0.153	0.236	
TEA	318	2382	0.608	0.124	0.155	
TEA	333	2363	0.474	0.105	0.095	
DMMEA	303	2387	0.812	0.183	0.103	
DMMEA	318	2368	0.597	0.141	0.059	
DMMEA	333	2346	0.469	0.105	0.032	
DEMEA	293	2369	1.032	0.346	0.379	
DEMEA	303	2354	0.820	0.258	0.207	
DEMEA	318	2332	0.602	0.178	0.121	
DEMEA	333	2305	0.472	0.130	0.069	

cording to relation 3 the COS solubility in aqueous amine solutions with fair accuracy. As illustrated by Figures 1 and 2 for aqueous ethylene glycol and aqueous sulfolane solutions, this COS–N_2O analogy is expected to hold only up to a certain maximum amine concentration. This maximum concentration until which the analogy holds is probably for COS lower than

Table VII. Solubility m of N_2O in Aqueous MEA Solutions

C/(mol·m^{-3})	T/K	m	C/(mol·m^{-3})	T/K	m
182.5	303	0.552	584.3	333	0.303
391.1	303	0.513	871.0	333	0.307
776.9	303	0.527	1579.1	333	0.305
1549.9	303	0.534	1765.1	333	0.314
2162.8	303	0.518	2592.8	333	0.314
3225.8	303	0.512	3309.1	333	0.302
3245.7	303	0.514	3701.2	333	0.335
197.1	318	0.366	211.3	348	0.263
415.2	318	0.379	422.0	348	0.277
874.8	318	0.380	885.7	348	0.269
1621.0	318	0.377	1796.8	348	0.271
2464.8	318	0.373	2669.1	348	0.270
3251.2	318	0.382	2888.5	348	0.296
3532.9	318	0.368	3644.2	348	0.295
233.0	333	0.304	3911.3	348	0.310

Table VIII. Solubility m of N_2O in Aqueous DGA Solutions

C/(mol·m^{-3})	T/K	m	C/(mol·m^{-3})	T/K	m
211.3	298	0.602	199.4	318	0.377
408.0	298	0.584	360.3	318	0.371
805.2	298	0.576	909.2	318	0.379
1611.7	298	0.561	1831.8	318	0.377
2440.9	298	0.525	2575.8	318	0.361
3239.3	298	0.491	3591.3	318	0.346
4673.4	298	0.459	3639.2	318	0.352
6127.7	298	0.402	200.8	333	0.301
6140.0	298	0.413	407.1	333	0.308
186.1	303	0.512	795.5	333	0.304
395.4	303	0.521	1711.5	333	0.299
794.7	303	0.528	2315.1	333	0.305
1627.9	303	0.491	2489.1	333	0.296
2277.2	303	0.487	3253.8	333	0.316
3245.8	303	0.453	3535.0	333	0.319
3255.7	303	0.441			

Table IX. Solubility m of N_2O in Aqueous DEA Solutions

C/(mol·m^{-3})	T/K	m	C/(mol·m^{-3})	T/K	m
244.4	303	0.502	675.0	318	0.375
302.0	303	0.517	812.5	318	0.367
598.8	303	0.501	1367.0	318	0.361
600.0	303	0.492	1520.1	318	0.370
796.8	303	0.509	2444.9	318	0.361
863.0	303	0.496	3385.0	318	0.344
1214.8	303	0.493	403.0	333	0.317
1733.3	303	0.482	835.5	333	0.324
2592.8	303	0.464	1698.1	333	0.319
3640.1	303	0.442	2445.5	333	0.317
265.8	318	0.373	3223.5	333	0.312
417.9	318	0.375			

Table X. Solubility m of N_2O in Aqueous MMEA Solutions

C/(mol·m^{-3})	T/K	m	C/(mol·m^{-3})	T/K	m
200.1	303	0.529	1511.3	318	0.390
489.6	303	0.493	2509.7	318	0.379
889.3	303	0.481	2810.5	318	0.372
1032.4	303	0.503	3047.0	318	0.383
1694.6	303	0.494	201.9	333	0.324
2094.4	303	0.457	393.7	333	0.322
2309.3	303	0.467	795.9	333	0.324
3115.8	303	0.447	1579.9	333	0.327
223.7	318	0.409	2408.9	333	0.334
400.8	318	0.401	3188.7	333	0.338
899.0	318	0.393	3232.1	333	0.333

for CO_2, as can be concluded from a comparison between the present data on a COS–N_2O analogy and data on a CO_2–N_2O analogy reported by Laddha et al. (*2*), Haimour and Sandall (*3*), and Oyevaar et al. (*13*).

3.2. Physical Data. Polynomial coefficients for the calculation of density and viscosity of aqueous amine solutions at various temperatures are reported in Tables V and VI, respectively. The present viscosity data can be used to estimate

Table XI. Solubility m of N_2O in Aqueous AMP and MOR Solutions at 303 K

amine	C/(mol·m^{-3})	m	amine	C/(mol·m^{-3})	m
AMP	192.6	0.518	MOR	203.0	0.527
AMP	391.8	0.513	MOR	475.3	0.520
AMP	767.6	0.505	MOR	777.2	0.512
AMP	1558.5	0.500	MOR	1588.2	0.538
AMP	1970.1	0.481	MOR	2189.9	0.539
AMP	2484.0	0.468	MOR	3112.0	0.515
AMP	3139.0	0.443	MOR	3244.0	0.530
AMP	3248.4	0.441			

Table XII. Solubility m of N_2O in Aqueous TEA Solutions

C/(mol·m^{-3})	T/K	m	C/(mol·m^{-3})	T/K	m
121.5	293	0.658	385.4	318	0.390
198.5	293	0.655	418.5	318	0.396
401.9	293	0.660	792.9	318	0.395
804.3	293	0.638	816.6	318	0.389
828.1	293	0.647	1593.9	318	0.383
1581.0	293	0.612	2370.6	318	0.374
1623.9	293	0.606	2419.9	318	0.371
3182.7	293	0.526	200.6	333	0.320
3193.0	293	0.526	394.9	333	0.312
395.3	303	0.530	407.9	333	0.308
415.8	303	0.525	776.4	333	0.312
765.4	303	0.514	1625.5	333	0.312
791.6	303	0.513	1647.7	333	0.306
2338.1	303	0.441	2408.4	333	0.311
2372.5	303	0.444	2426.8	333	0.307
208.5	318	0.397			

Table XIII. Solubility m of N_2O in Aqueous DMMEA Solutions

C/(mol·m^{-3})	T/K	m	C/(mol·m^{-3})	T/K	m
210.7	303	0.525	805.5	318	0.395
397.2	303	0.539	1552.9	318	0.388
408.7	303	0.526	1580.9	318	0.393
858.1	303	0.517	2361.3	318	0.386
879.2	303	0.513	2383.8	318	0.397
1479.5	303	0.493	394.7	333	0.316
1516.3	303	0.511	401.4	333	0.319
2340.6	303	0.479	780.2	333	0.310
2382.5	303	0.477	791.0	333	0.308
210.6	318	0.400	1568.5	333	0.319
384.1	318	0.401	1584.9	333	0.309
398.7	318	0.400	2370.9	333	0.338
796.0	318	0.398	2496.4	333	0.334

diffusivities via a Stokes–Einstein relationship (*9*).

Solubilities of N_2O in various aqueous amine solutions at various temperatures are presented in Table VII (MEA), Table VIII (DGA), Table IX (DEA), Table X (MMEA), Table XI (AMP, Morpholine), Table XII (TEA), Table XIII (DMMEA), and Table XIV (DEMEA). The N_2O solubilities reported in Tables VII–XIV were summarized by means of best-fit polynomials: polynomial coefficients are reported in Table XV.

The agreement between the present data and the limited amount of data reported by Haimour (*16*) for the N_2O solubility in aqueous DEA solutions at 303 K is rather poor. However, for the solubility of N_2O in water, some significant discrepancies also exist between the data published by Haimour (*16*) and the experimental and literature data compiled by Versteeg and Van Swaaij (*9*). For aqueous TEA solutions at 293, 303, and 313 K, Sotelo et al. (*17*) published CO_2 solubility data which were calculated from experimental N_2O data via the CO_2–N_2O analogy. The present data are in accordance with the data of Sotelo et al. (*17*).

In Tables XVI and XVII, N_2O solubility data at 298 K are presented for aqueous blends of DIPA with tertiary amines and DEA with tertiary amines. Density and viscosity of these blends are also given.

Density, viscosity, N_2O solubility and N_2O diffusivity at 298 K for various mixtures of MDEA, water, and ethanol are presented

Table XIV. Solubility m of N_2O in Aqueous DEMEA Solutions

C/(mol·m^{-3})	T/K	m	C/(mol·m^{-3})	T/K	m
202.5	293	0.666	787.6	318	0.396
403.7	293	0.655	804.7	318	0.402
801.5	293	0.629	1575.4	318	0.405
811.4	293	0.631	1597.7	318	0.403
1606.3	293	0.584	2359.9	318	0.429
1608.3	293	0.582	2361.8	318	0.423
2434.0	293	0.567	149.4	333	0.312
198.8	303	0.534	205.4	333	0.304
206.9	303	0.537	300.4	333	0.307
409.9	303	0.517	603.3	333	0.319
809.6	303	0.508	787.3	333	0.301
1455.2	303	0.507	1440.0	333	0.337
1649.1	303	0.489	1519.6	333	0.334
2406.6	303	0.497	1760.6	333	0.356
2414.3	303	0.500	2272.3	333	0.384
196.7	318	0.400	2277.7	333	0.391
400.0	318	0.398			

Table XV. Polynomial Coefficients for the Calculation of the N_2O Solubility m in Aqueous Alkanolamine Solutions of Concentration C at Various Temperatures [$m = c_0 + c_1(C/(\text{mol}\cdot\text{m}^{-3})) + c_2(C^2/(\text{mol}^2\cdot\text{m}^{-6})) + c_3(C^3/(\text{mol}^3\cdot\text{m}^{-9}))$]

amine	T/K	C_{max}/(mol·m^{-3})	c_0	10^3c_1	10^6c_2	10^9c_3
MEA	303	3246	0.541	−0.008		
MEA	318	3378	0.389			
MEA	333	3701	0.304	0.002		
MEA	348	3911	0.261	0.010		
DGA	298	6140	0.605	−0.032		
DGA	303	3256	0.538	−0.024		
DGA	318	3639	0.383	−0.010		
DGA	333	3535	0.304			
DEA	303	3640	0.522	−0.020		
DEA	318	3385	0.384	−0.011		
DEA	333	3224	0.316	−0.001		
MMEA	293	2626	0.692	−0.004	−0.010	
MMEA	303	3762	0.533	−0.019		
MMEA	318	3389	0.402	−0.008		
MMEA	333	3232	0.317	0.007		
AMP	303	3248	0.533	−0.027		
MOR	303	3605	0.526	−0.003		
TEA	293	3193	0.678	−0.047		
TEA	303	2373	0.547	−0.045		
TEA	318	2420	0.404	−0.032	0.024	−0.007
TEA	333	2427	0.310	−0.001		
DMMEA	303	2383	0.541	−0.027		
DMMEA	318	2396	0.400	−0.003		
DMMEA	333	2496	0.310	−0.004	0.005	
DEMEA	293	2434	0.684	−0.077	0.011	
DEMEA	303	2444	0.544	−0.071	0.036	−0.006
DEMEA	318	2362	0.402	−0.002	−0.008	0.005
DEMEA	333	2278	0.308	−0.010	0.020	

in Table XVIII. The diffusivities obtained for CO_2 in water/ethanol mixtures are in fair agreement with the diffusivity data reported by Simons and Ponter (*18*) and Takahashi and Kobayashi (*19*). It should be noted that, in contradiction to aqueous amine systems (*9*), the diffusivities for N_2O in the ternary system MDEA/water/ethanol cannot be described by a Stokes–Einstein relationship.

4. Conclusions

From the present work it can be concluded that an analogy between COS and N_2O with respect to solubilities is valid for aqueous solutions of ethylene glycol and sulfolane up to concentrations of about 25 mass %. For engineering purposes, this seems to justify the application of a COS–N_2O analogy for the calculation of COS solubilities in diluted aqueous amine solutions.

Solubility data for COS in water at temperatures ranging from 298 to 338 K have been presented. Together with previously

Table XVI. Physical Constants for DIPA–Tertiary Amine Mixtures

DIPA/(mol·m^{-3})	tertiary amine	C_{R_3N}/(mol·m^{-3})	C_{H_2O}/(mol·m^{-3})	ρ/(kg·m^{-3})	η/(10^{-3} Pa·s)	m_{N_2O}
231	TEA	990	46700	1020.0	1.66	0.560
243	TEA	1971	39830	1044.2	2.99	0.534
250	TEA	2743	34430	1062.9	5.02	0.492
254	TEA	3407	29630	1076.1	8.34	0.474
338	MDEA	998	47020	1011.2	1.70	0.570
348	MDEA	2085	40390	1022.6	2.85	0.519
337	MDEA	2749	36500	1030.1	4.36	0.492
381	MDEA	3517	31570	1038.8	7.26	0.458
798	MDEA	506	46760	1009.1	1.82	0.554
798	MDEA	1515	40750	1021.0	3.10	0.510
799	MDEA	2502	34790	1031.4	5.49	0.470
954	DMMEA	1003	43630	1002.8	2.45	0.529
957	DMMEA	1498	41110	1001.8	3.08	0.510
988	DMMEA	1977	38430	1000.8	3.66	0.494
946	DMMEA	2500	36070	998.8	4.77	0.473
876	DMMEA	3200	33070	993.9	4.89	0.477
1002	DEMEA	500	45090	1004.5	2.21	0.546
1006	DEMEA	1007	41690	1003.1	3.04	0.503
1015	DEMEA	1998	34870	997.7	5.47	0.514
1005	DEMEA	2502	31420	993.2	7.23	0.535
978	DEMEA	2973	28230	986.9	7.73	0.614
1025	DEMEA	4028	20220	973.0	15.88	0.781

Table XVII. Physical Constants for DEA–Tertiary Amine Mixtures

DEA/(mol·m^{-3})	tertiary amine	C_{R_3N}/(mol·m^{-3})	C_{H_2O}/(mol·m^{-3})	ρ/(kg·m^{-3})	η/(10^{-3} Pa·s)	m_{N_2O}
205	TEA	970	47520	1022.5	1.55	0.564
208	TEA	1982	40330	1044.4	2.79	0.520
229	TEA	2978	33190	1066.5	5.51	0.487
511	TEA	991	45730	1025.4	1.76	0.545
518	TEA	2999	31530	1070.1	6.60	0.468
207	MDEA	1036	48155	1012.0	1.51	0.542
200	MDEA	2055	42131	1024.1	2.51	0.520
192	MDEA	3051	36137	1033.9	4.51	0.492
501	MDEA	1037	46620	1015.7	1.77	0.544
483	MDEA	3091	34385	1038.0	5.40	0.481
501	DMMEA	1002	47706	1000.1	1.52	0.584
491	DMMEA	1963	42847	997.0	2.33	0.545
495	DMMEA	2990	37570	995.6	3.80	0.488
994	DMMEA	1003	45080	1006.3	1.93	0.563
974	DMMEA	1949	40405	1004.5	2.85	0.532
1081	DMMEA	3074	34050	1001.3	4.95	0.480
498	DEMEA	500	49410	1001.4	1.40	0.572
546	DEMEA	1066	45510	1002.3	1.89	0.557
526	DEMEA	2517	35650	992.8	4.59	0.544
1024	DEMEA	759	44990	1007.3	2.01	0.561
994	DEMEA	994	43602	1006.7	2.28	0.546
994	DEMEA	1501	40210	1005.0	4.06	0.529
1019	DEMEA	2497	33250	998.9	5.74	0.531

Table XVIII. Physical Data for the MDEA/H_2O/Ethanol Systems at 298 K[a]

C_{MDEA}/(mol·m^{-3})	C_{H_2O}/(mol·m^{-3})	$C_{ethanol}$/(mol·m^{-3})	ρ/(kg·m^{-3})	η/(10^{-3} Pa·s)	gas	m	$mD^{1/2}$/(10^{-5} m·s$^{-0.5}$)	ref
0	7070	15290	832.3	1.78	CO_2	2.21	10.3	present work
							12*	18
							8.3*	19
					N_2O	2.19	11.0	present work
1060	6540	13300	858.0	2.51	N_2O	2.13	9.22	present work
1990	5770	11820	881.0	3.54	N_2O	2.03	7.80	present work
3050	4540	10020	906.4	5.34	N_2O	1.93	6.92	present work
0	14550	13090	865.3	2.19	CO_2	1.64	6.80	present work
							7.8*	18
							5.4*	19
					N_2O	1.54	6.23	present work
1060	12730	11530	886.3	3.02	N_2O	1.51	5.94	present work
1920	11360	10280	907.3	4.27	N_2O	1.43	5.39	present work
3100	9670	8460	933.0	6.85	N_2O	1.39	4.51	present work
0	28790	8840	925.8	2.70	CO_2	1.05	3.67	present work
							4.1*	18
							3.8*	19
					N_2O	0.88	3.30	present work
1040	22930	8570	936.3	3.64	N_2O	0.88	3.12	present work
2020	20290	7470	950.0	5.16	N_2O	0.87	2.82	present work
3180	16930	6160	966.9	8.07	N_2O	0.88	2.31	present work

[a] Numbers marked with an asterisk are interpolated values.

published data, these data were summarized by an Arrhenius relationship.

Extensive data have been reported for density, viscosity, N_2O solubility, and N_2O diffusivity for various aqueous amine solutions, aqueous mixtures of alkanolamines, and solutions of MDEA in water/ethanol.

Acknowledgment

We acknowledge C. v. d. Beek, M. v. Dijk, W. Lengton, W. Leppink, R. v. d. Meer, A. Montanaro, L. Pirrone, and J. Sijm for their respective parts in the experimental work.

Glossary

C	concentration
D	diffusivity
Ha	Hatta number (see eq 2)
k_{app}	apparent pseudo-first-order reaction rate constant
k_L	liquid-phase mass-transfer coefficient
m	dimensionless solubility (see eq 4)
T	temperature

Greek Letters

η	viscosity
ρ	density

Amine Abbreviations

AMP	2-amino-2-methyl-1-propanol
DEA	diethanolamine
DEMEA	diethylmonoethanolamine
DGA	diglycolamine, 2-(2-aminoethoxy)ethanol
DIPA	diisopropanolamine
DMMEA	dimethylmonoethanolamine
MDEA	*N*-methyldiethanolamine
MEA	monoethanolamine
MMEA	methylmonoethanolamine
MOR	morpholine, 1-oxa-4-azacyclohexane
TEA	triethanolamine

Registry No. COS, 463-58-1; CO_2, 124-38-9; N_2O, 10024-97-2; MEA, 141-43-5; DEA, 111-42-2; MMEA, 109-83-1; AMP, 124-68-5; TEA, 102-71-6; MDEA, 105-59-9; DMMEA, 108-01-0; DEMEA, 100-37-8; DGA, 929-06-6; morpholine, 110-91-8; sulfolane, 126-33-0.

Literature Cited

(1) Kohl, A. L.; Riesenfeld, F. C. *Gas Purification*, Gulf Publishing Co.: Houston, TX, 1979.
(2) Laddha, S. S.; Diaz, J. M.; Danckwerts, P. V. *Chem. Eng. Sci.* **1981**, *36*, 228-229.
(3) Haimour, N.; Sandall, O. C. *Chem. Eng. Sci.* **1984**, *39*, 1791-1796.
(4) Al-Ghawas, H. A.; Ruiz-Ibanez, G.; Sandall, O. C. *Chem. Eng. Sci.* **1989**, *44*, 631-639.
(5) Philipp, B.; Dautzenberg, H. *Z. Phys. Chem.* **1965**, *229*, 210-224.
(6) Blauwhoff, P. M. M.; Versteeg, G. F.; van Swaaij, W. P. M. *Chem. Eng. Sci.* **1984**, *39*, 207-225.
(7) Versteeg, G. F.; van Swaaij, W. P. M. *Chem. Eng. Sci.* **1988**, *43*, 573-587.
(8) Littel, R. J.; van Swaaij, W. P. M.; Versteeg, G. F. *AIChE J.* **1990**, *36*, 1633-1640.
(9) Versteeg, G. F.; van Swaaij, W. P. M. *J. Chem. Eng. Data* **1988**, *33*, 29-34.
(10) Nijsing, R. A. T. O.; Hendriksz, R. H.; Kramers, H. *Chem. Eng. Sci.* **1959**, *10*, 88-104.
(11) Littel, R. J.; van Swaaij, W. P. M.; Versteeg, G. F. AIChE Meeting, Orlando, FL, 1990.
(12) Siggia, S.; Hanna, J. G.; Kervenski, I. R. *Anal. Chem.* **1950**, *12*, 1295-1297.
(13) Oyevaar, M. H.; Morssinkhof, R. W. J.; Westerterp, K. R. *J. Chem. Eng. Data* **1989**, *34*, 77-82.
(14) Sharma, M. M. *Trans. Faraday Soc.* **1965**, *61*, 681-688.
(15) Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds-Binary Systems*; Pergamon Press: New York, 1963; Vol. 1.
(16) Haimour, N. M. *J. Chem. Engng. Data* **1990**, *35*, 177-178.
(17) Sotelo, J. L.; Benitez, F. J.; Beltran-Heredia, J.; Rodriguez, C. *AIChE J.* **1990**, *36*, 1263-1266.
(18) Simons, J.; Ponter, A. B. *J. Chem. Eng. Jpn.* **1975**, *8*, 347-350.
(19) Takahashi, M.; Kobayashi, Y. *J. Chem. Eng. Data* **1982**, *27*, 328-331.

Received for review February 21, 1991. Accepted August 9, 1991. These investigations were supported by the Koninklijke/Shell Laboratorium Amsterdam, The Netherlands.

Excess Volumes of Mixtures of Alkanes with Carbonyl Compounds

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Excess volumes of mixing were measured at 20 °C for mixtures of three linear alkanes (hexane, heptane, and octane) and cyclohexane with five alkyl acetates (methyl, ethyl, propyl, butyl, and amyl acetates) and two ketones (acetone and 2-butanone). The whole composition range was studied for all 28 binary systems. For a given alkane, the excess volume decreases with the increasing size of the carbonyl compound. For a given carbonyl compound, the excess volume increases with the size of the alkane. The excess volumes for a given pair are distinctly larger for mixtures dilute in the carbonyl compound than for mixtures dilute in the alkane component. This is a result of the nonregular nature of mixtures of compounds having strongly interacting dipoles with nonpolar alkanes.

Among the excess thermodynamic functions of mixing, the excess volume of mixing is understood the least, yet it may reveal details of molecular interaction in liquid mixtures that are manifested by other thermodynamic properties to a minor extent or not at all. In our laboratory, we are accumulating extensive thermodynamic data concerning mixtures and utilizing the methods of densitometry, calorimetry, light scattering, and inverse gas chromatography (*1*, *2*). The experiments are performed under very consistent conditions that allow extensive

Table I. Densities ρ of Pure Solvents at 20 °C

solvent	ρ/(g cm^{-3}) this work	ρ/(g cm^{-3}) lit.
methyl acetate	0.933 89	0.9342 (*3*)
ethyl acetate	0.900 96	0.9003 (*3*)
propyl acetate	0.887 58	0.8883 (*3*)
butyl acetate	0.881 68	0.8813 (*3*)
amyl acetate	0.877 76	0.8766 (*3*)
acetone	0.791 38	0.7898 (*4*)
2-butanone	0.805 61	0.8049 (*4*)
hexane	0.659 87	0.6594 (*5*)
heptane	0.684 03	0.6838 (*6*)
octane	0.702 78	0.7025 (*7*)
cyclohexane	0.778 84	0.7786 (*8*)

0021-9568/92/1737-0055$03.00/0